CHARACTERIZATION OF IMPREGNATED COMMERCIAL RICE HUSKS ACTIVATED CARBON WITH MONOETHANOLAMINE (MEA) AND DIETHANOLAMINE (DEA) AS POTENTIAL CO_2 ADSORBENT

SITI NORAISHAH BINTI MASOUM RAMAN

A thesis submitted in fulfilment of the
requirements for award of the degree of
Bachelor of Chemical Engineering

Faculty of Chemical Engineering & Natural Resources
Universiti Malaysia Pahang

JULY 2014

PENCIRIAN PERCANTUMAN KARBON AKTIF SEKAM PADI KOMERSIAL DENGAN MONOETANOLAMINA (MEA) DAN DIETANOLAMINA (DEA) YANG BERPOTENSI SEBAGAI PENJERAP KARBON DIOKSIDA

ABSTRAK

Kajian daripada pencirian percantuman karbon aktif dengan monoethanolamine (MEA) dan dietanolamina (DEA) sebagai kebolehan penjerap karbon dioksida (CO_2) telah dijalankan. Kapasiti penjerapan karbon aktif boleh ditingkatkan dengan memperkenalkan kumpulan amina pada permukaan bahan penjerap tersebut. MEA dan DEA telah dipilih sebagai sebatian amino untuk proses percantuman permukaan karbon aktif. Sintesis karbon aktif yang tercantum telah disediakan mengikut kepekatan dan nisbah campuran. Ciri fizikokimia karbon aktif yang tercantum telah disifatkan oleh *X-Ray Diffraction* (XRD), *Brunauer, Emmett and Teller* (BET), *Fourier Transform Infrared Spectroscopy* (FTIR) dan *Field Emission Scanning Electron Microscopy* (FESEM). Analisis XRD telah digunakan untuk menentukan kehadiran jenis sebatian pada permukaan karbon aktif. Hasil kajian menunjukkan bahawa sudut pembelauan sekitar 21.66º 22.18º yang dihubungkan untuk pyrazole, ethanolamine dan dietanolamina membuktikan kehadiran hidrokarbon dan amina pada permukaan karbon aktif. Daripada analisis BET, jumlah luas permukaan dan isipadu liang menurun dengan peningkatan kepekatan MEA dan DEA. Kehadiran kumpulan amida dalam analisis FTIR pada jalur 3288 cm^{-1} dan 1651 cm^{-1} untuk karbon aktif yang tercantum membuktikan terdapat satu tindak balas berlaku antara kumpulan karboksil pada permukaan karbon aktif dengan amina terikat. Bagi analisis FESEM, ia menunjukkan bahawa morfologi karbon aktif tanpa cantuman mengandungi banyak liang di permukaannya manakala liang di karbon aktif tercantum dengan MEA dan DEA telah dipenuhi dengan amina mengikut kepekatan yang dipilih. Penemuan dari penyelidikan ini memberitahu terdapat potensi yang tinggi untuk kapasiti penjerapan CO_2 apabila hasil pencirian menunjukkan maklum balas yang positif terhadap kuantiti MEA dan DEA dalam sampel percantuman karbon aktif.

CHARACTERIZATION OF IMPREGNATED COMMERCIAL RICE HUSKS ACTIVATED CARBON WITH MONOETHANOLAMINE (MEA) AND DIETHANOLAMINE (DEA) AS POTENTIAL CO_2 ADSORBENT

ABSTRACT

The studies characterization of impregnated activated carbon with monoethanolamine (MEA) and diethanolamine (DEA) as potential carbon dioxide (CO_2) adsorbent was successfully performed. The adsorption capacity of the activated carbon can be increased by introducing the amine group on the surface of the adsorbent. MEA and DEA were selected as amino compounds for the binding process on the activated carbon surface. The synthesis of the impregnated activated carbon was prepared according to the concentration and mixture ratio. The physicochemical properties of the impregnated activated carbon were characterized by X-Ray Diffraction (XRD), Brunauer, Emmett and Teller (BET), Fourier Transform Infrared Spectroscopy (FTIR) and Field Emission Scanning Electron Microscopy (FESEM). The XRD analysis was used to determine the type of compound presence on the activated carbon surface. The result reveals that the diffraction angles around 21.66º to 22.18º were linked for pyrazole, ethanolamine and diethanolamine which prove the presence of hydrocarbon and amine on the activated carbon surfaces. From the BET analysis, the total surface area and pore volume decreased with the increase of concentration of MEA and DEA. The presence of amide functional groups in FTIR analysis at 3288 cm^{-1} and 1651 cm^{-1} band for the impregnated activated carbon proved that there was a reaction occurs between carboxyl groups on the activated carbon surfaces with amine bonded. As for FESEM analysis, it was shown that the morphology of the non-impregnated activated carbon contains many pores on its surface while the pores on the impregnated activated carbon with MEA and DEA were filled with amines according to the selected concentration. The findings signify the high potential of CO_2 adsorption capacity as the characterization results shows a positive feedback towards the quantity of MEA and DEA in the impregnated activated carbon samples.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

AC	Activated carbon
BET	Brunauer, Emmett and Teller isotherm
DEA	Diethanolamine
FESEM	Field Emission Scanning Electron Microscopy
FTIR	Fourier Transform Infrared Spectroscopy
MEA	Monoethanolamine
XRD	X-Ray Diffraction

LIST OF SYMBOLS

^{o}	Degree.
C	Constant value, characteristics of the adsorbate.
N_A	Avogadro constant.
m	Mass of test powder.
θ	Fraction of surface of covered by adsorbed molecules.
P	Gas pressure.
P_0	Saturated pressure of adsorbate gas.
S	Surface area of solid.
V_a	Volume of gas adsorbed at standard temperature and pressure.
V_m	Volume of gas adsorbed at STP to produce an apparent monolayer on the sample surface.

LIST OF APPENDICES

CHAPTER 1

INTRODUCTION

The topic for this research is Characterization of Impregnated Commercial Rice Husks Activated Carbon with Monoethanolamine (MEA) and Diethanolamine (DEA) as Potential CO_2 Adsorbent. Activated carbon is a form of carbon processed which is known to have a large surface area for adsorption process. This research investigates the characterization of activated carbon for adsorption process with and without the aid of MEA and DEA.

1.1 Background of Study

Global warming is the term used to describe a gradual increase in the average temperature of the Earth's atmosphere and its oceans, a change that is believed to be permanently changing the Earth's climate. The major contribution of this problem is because of the release of acidic gases such as carbon dioxide (CO_2), sulphur dioxide (SO_2) and hydrogen sulphide (H_2S) from human's activity like industrial revolution and destruction of forests. U.S. Department of State (2007) states that many industrial processes emit CO_2 through fossil fuel combustion and several processes produce CO_2 emissions through chemical reactions that do not involve combustion, for example, the production and consumption of mineral products such as cement, the production of metals such as iron and steel, and the production of chemicals. By increasing the concentration of CO_2 gases, the infrared energy emitted by the surface will be increased and being absorbed by the atmosphere. The extra energy from the warmer atmosphere will radiates back to the Earth's surface thus, increase the surface temperature.

The present of adsorbent may help in reducing the CO_2 level in the atmosphere. In commercial processes, the adsorbent is usually in the form of small particles (solid) in a fixed bed and the fluid (liquid or gas) passed through the bed before being adsorbed by the solid particles (Geankoplis, 2003). Adsorption is systematic in most natural physical, biological, and chemical aspect, and is widely used in industrial applications such as activated charcoal, synthetic resins and water purification. There are many types of physical and chemical adsorbent that can be used to adsorb acidic gas such as activated carbons and zeolites for physical adsorbent while alkali metal carbonates and amine-based material for chemical adsorbent. Zeolites have a high capacity for CO_2 capture but it is expensive whereas carbon-based materials are abundant, cheap, easy to make, and chemically and hydrothermally stable, but their selectivity for CO_2 is low in the presence of other gases such as Nitrogen (N_2), Hydrogen (H_2) and Methane (CH_4) (Wang et al., 2010). However, the basic amine group is an ideal functionality to strongly interact with acidic CO_2 molecules (Lin et al., 2013).

There are many primary raw materials that have high carbon content that can be used as activated carbon such as coal, wood, palm shell and coconut shell. Activated carbon is the most versatile and frequently used sorbent for environmental control in the form of a fixed bed due to its large internal surface area and pore volume, and its ability to adsorb organic vapors at low cost (Jahangiri et al., 2013). The huge surface area of activated carbon gives it many bonding sites which can be used to trapped chemical for adsorption process. The carbon-based material is converted to activated carbon by thermal decomposition in a furnace using a controlled atmosphere and heat (Deithorn & Mazzoni, 2013). The heating process is called pyrolysis which means thermochemical decomposition of organic material at elevated temperatures in the absence of oxygen (or any halogen).

One of the carbon-based materials that can be used as activated carbon is rice husk. Rice husk is one of the main agriculture wastes in many rice producing countries. Rice husk is the outermost layer of paddy grain which is produced in the first step of milling process and makes up about 20% of the rice (paddy). The rice husk is then undergoing the activation process with used of furnace and steam boiler to become an activated carbon. In Malaysia, the production of rice is increases annually from 2.7 million tonnes in 1985 to 4 million tonnes in 2009 because of the increasing population (Arshad et al., 2011). With the high number of rice produced, the rice husk activated carbon production will also be increased.

1.2 Problem Statement

Acidic gases such as CO_2 gas can lead to environmental problem such as greenhouse effect and global warming. The CO_2 gas does not only elevate global temperature; it also gives negative impact to human health because its higher concentrations can affect respiratory function and thus, resulting in lower concentrations for breathing (Subki et al., 2011). Therefore it is important to control the release of CO_2 gas to the atmosphere to minimise the environmental problem. The rice husk ash, if properly been treated can be a good source of activated carbon that can be used to adsorb the CO_2 gas. In Malaysia, the production of rice is increases annually as the demand for rice is increasing within country and outside the country. Generally, farmers and rice processor often burn the rice husk as wastes and most of the rice husks are not commercially used. Burning of rice husk in ambient atmosphere leaves a residue, called rice husk ash which will cause damage to land and surrounding area where it is dumped (Kumar et al., 2012).

1.3 Research Objective

The objective of this research is to study the comparison between the non-impregnated activated carbon with the impregnation of MEA and DEA with activated carbon at different concentration and mixture ratio.

1.4 Scopes of Study

The activated carbon being used in this research is made from rice husk ash. The rice husk ash is produced with used of furnace and steam boiler. The research is conducted according to three main variables that is the absent of MEA and DEA with activated carbon, impregnation of MEA and DEA with activated carbon at different concentration and impregnation of MEA and DEA mixture with activated carbon at different mixture ratio. The characterization of the activated carbon with and without the impregnation of MEA and DEA will be observe by using several methods such as X-Ray Diffraction (XRD) analysis, Brunauer, Emmett and Teller's (BET) isotherm, Fourier Transform Infrared Spectroscopy (FTIR) analysis and Field Emission Scanning Electron Microscopy (FESEM) analysis.

1.5 Significance of Study

This research is done to produce an adsorbent from the rice husk activated carbon. The activated carbon is impregnated with MEA and DEA to increase the adsorption capacity of acidic gases such as CO_2. The adsorption of these acidic gases will help to reduce the environmental problem such as global warming greenhouse effect. The study is done with different concentration and mixture ratio of MEA and DEA to identify the optimum concentration and mixture ratio of the adsorbent that going to be used. This research provides several benefits such as reduce the amount of acidic gas in air and improve the environment air quality. With a good quality of air, human health and environment problems can be reduced. It is hope that this research may give a good impact for environment, especially and therefore, will give benefits to the community.

CHAPTER 2

LITERATURE REVIEW

This chapter provides the general ideas on the subject that are going to be study including the background and introduction of rice husk, activated carbon as adsorbent, impregnation of activated carbon with amine and characterization of impregnated and non-impregnated activated carbon.

2.1 Rice Husk as Activated Carbon

Each year, approximately 600 million tons of rice paddy is produced globally and there are more than seventy countries in the world produce rice including China, India, and Indonesia (Kumar et al., 2013). 20% of the rice paddy is husk, giving an annual total production of 120 million tons (Shelke et al., 2010). Rice husk is a by-product of the rice milling process and usually treated as agricultural waste (Kermani et al., 2006). Rice husks are the hard protecting coverings of grains of rice which is made from hard materials such as opaline silica and lignin in order to protect the seed during the growing season (Subki et al., 2011). The presence of large amount of hydrocarbon such as cellulose and lignin content made the rice husk to be used as a raw material for preparation of activated carbons that contain complex porous structures (Kumar et al., 2012). The high silica content also contributes the formation of residual carbon in the rice husk (Javed et al., 2010). Porous carbon derived from the rice husks has wide availability, has fast kinetics and appreciable adsorption capacities too (Chen et al., 2011). At the temperature from 500 to 700°C, rice husk may be carbonized for a certain period of time and after the thermal decomposition, rice husk would become granular charcoal (Chien, C. C., 2013). The thermal decomposition enables the formation of pores on the surface of the activated carbon. An increase on number of pores and the size of pores made the surface area of the activated carbon larger. According to Allwar (2012), an activated carbon usually consists of three types of pores which are micropores (diameter < 2 nm), mesopores (diameter 2 – 50 nm), and macropores (diameter $>$ 50 nm). The function of micropores and mesopores is to give the carbon its adsorptive capacity whereas micropores allow the access of adsorbate into the micropores and mesopores (Mdoe & Mkayula, 2002). The rice husk that has been processed as activated carbon can be used widely in many applications such as chemical adsorbent and fuel in power plant. The high availability and low price makes extra benefit towards the use of this material in many industries.

2.2 Activated Carbon as Adsorbent

Gas adsorption is a separation process in which a gaseous component is separated from a gas stream with the use of a solid material known as adsorbent (Spigarelli & Kawatra, 2013). Activated carbon is usually used as adsorbent for environmental control in the form of a fixed bed due to its large internal surface area and pore volume, and its ability to adsorb organic vapors at low cost (Jahangiri et al., 2013). Specific surface area, size and porosity are some of the physical properties of carbons while surface functional groups such as carboxyl and anhydrides are the chemical properties of activated carbon (Meng et al., 2009). Large surface area is a result of creation of additional micropores and probably widening of the existing one, hence, increase in active sites as well as accessibility to the sites (Mdoe & Mkayula, 2002). The types of activated carbon that usually being used as adsorbent is granular (0.2 – 5 mm) and palletised (> 5 mm) because of their low pressure drop and high mechanical strength (Dali et al., 2012). Activated carbon has a very large pore volume especially in the mesopore range resulting from the activation process. Activation process of carbon would tend to increase the number of active sites, and in turn the surface activity, similar to observed reactions with higher activates (Cameron Carbon Incorporated, 2006). Physical adsorption occurs when weak Van der Waals force of attraction hold the organic molecules on the surface and in the pores of the adsorbent and is generally characterized by low heat absorption (Ray & Altshuer, 2013). Harmful gas such as CO_2 and H_2S is usually being adsorbed before released to the atmosphere. Adsorption is considered to be one of the most promising methods of mitigating fossil fuel CO_2 emissions and it has accepted recently nationwide (Snape et al., 2004). CO_2 gas is known as the major greenhouse gas which means it absorbs and emits radiation in the infrared range. The CO_2 gas does not only increase global temperature; it also gives drawbacks to human health because its higher concentrations can affect respiratory function and thus, resulting in lower concentrations for breathing (Subki et al., 2011). Therefore it is important to adsorb the harmful gas especially CO_2 gas before it been released to the atmosphere to minimise the environmental problem.

2.3 Impregnation of Amine with Activated Carbon

Carbon-based materials are abundant, cheap, easy to make, and chemically and hydrothermally stable, but their selectivity for CO_2 and other acidic gases is low in the presence of other gases such as N_2, H_2 and CH_4 (Wang et al., 2010). The carbon-based materials sorption capacity can be improved by using amine solution as the impregnator of the porous materials as the amine is characterized by a high absorption capacity in relation to CO_2 (Bukalak et al., 2013). CO_2 adsorption capacity also can be enhanced by impregnation of amine and ammonia on the surface of adsorbent (Boonpoke et al., 2011). The carbon based material is high in alkalinity and the amine will be stabilized on the surface so that the amine can be prevented from dissociating (Liang et al., 1995). In the direct method, amine will condense with carboxyl group on the activated carbon to form amide which is used in CO_2 captured (Houshmand et al., 2011). The impregnation of large amounts of amines is good on the mesoporous carbons having high surface area, large pore volumes and specific surface properties (Wang et al., 2012). The common amine used to make adsorbent is MEA, DEA and Polyethlenimine and Piperazine. Aqueous solutions of amines such as MEA have been used by industry as absorbents for acid gas such as CO_2 and H_2S (Drage et al., 2006). However, liquid amine is not a good choice for absorbent of the acidic gas as it needs high cost and creates several issues such as solvent leakage and corrosion. The integration of organic amines into porous material such as activated carbon may help to reduce these problems. Solid-supported amine sorbents offer many advantages for CO_2 capture such as potential elimination of corrosion problems and lower energy cost for sorbent regeneration (Qi et al., 2010). The impregnated activated carbon with MEA would develop many active sites on the surface and inside the pores of the activated carbon particles through chemisorption, thus the probability to adsorb CO_2 molecules is higher (Khalil et al., 2011). DEA is a secondary amine and superior absorbents compared to MEA, a primary amine (Warudka, S. S., 2011). According to Kim et. al. (2013), the breakthrough curve of MEA absorption rate is more than DEA absorption rate. This means that the DEA absorption rate and capacities is faster than MEA.

2.4 Impregnated and Non-Impregnated Activated Carbon

In the previous research, it is shown that impregnated activated carbon has a higher adsorption capacity than the non-impregnated activated carbon. Jahangiri et al. (2013) stated that the activated carbon impregnated with a nickel nitrate catalyst precursor and carbon nanofibers lasted about 50% longer than those activated carbon alone with a same weight of adsorbent. Activated carbon consists of acidic and basic surfaces. Figure 1 shows the acidic groups and basic groups on the surface of activated carbon.